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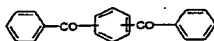
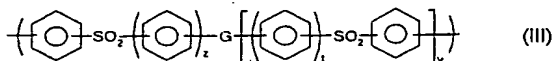
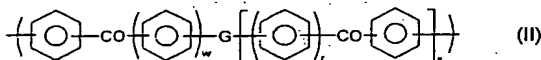
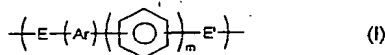
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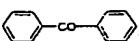
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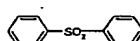
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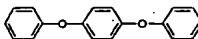
(i)*



(i)



(ii)



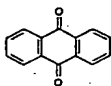
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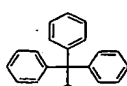
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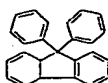
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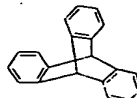
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(ix)



(x)

(57) Abstract: A composite membrane for use as an ion-exchange membrane includes a conductive polymer and a support material for the polymer, said polymer having a moiety of formula (I) and/or a moiety of formula (II) and/or a moiety of formula (III), wherein at least some of the units I, II and/or III are functionalized to provide ion exchange sites; wherein the phenyl moieties in units I, II, and III are independently optionally substituted and optionally cross-linked; and wherein m, r, s, t, v, w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from one of the following moieties (i)*, (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties.

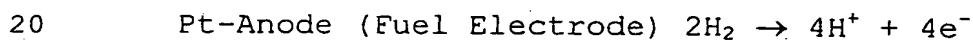
COMPOSITE ION-EXCHANGE MEMBRANES

This invention relates to a composite ion-exchange membrane and provides such a membrane per se and a method
5 of making such a membrane.

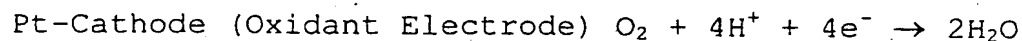
One type of known polymer electrolyte membrane fuel cell (PEMFC), shown schematically in Figure 1 of the accompanying diagrammatic drawings, may comprise a thin
10 sheet 2 of a hydrogen-ion conducting Polymer Electrolyte Membrane (PEM) sandwiched on both sides by a layer 4 of platinum catalyst and an electrode 6. The layers 2, 4, 6 make up a Membrane Electrode Assembly (MEA) of less than 1mm thickness.

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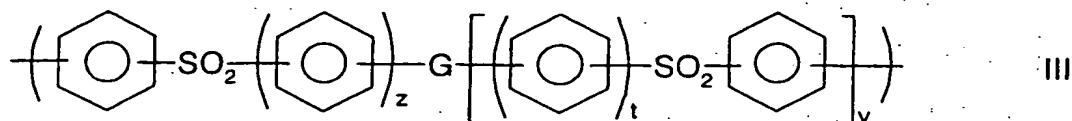
In a PEMFC, hydrogen is introduced at the anode (fuel electrode) which results in the following electrochemical reaction:



The hydrogen ions migrate through the conducting PEM to the cathode. Simultaneously, an oxidant is introduced at the cathode (oxidant electrode) where the following
25 electrochemical reaction takes place:



Thus, electrons and protons are consumed to produce
30 water and heat. Connecting the two electrodes through an external circuit causes an electrical current to flow in the circuit and withdraw electrical power from the cell.



wherein at least some of the units I, II and/or III are functionalized to provide ion exchange sites; wherein the phenyl moieties in units I, II, and III are independently optionally substituted and optionally cross-linked; and

5 wherein m, r, s, t, v, w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from

10 one of the following moieties (i)*, (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties

quaternary-aminoalkylated or chloromethylated, and optionally further modified to yield $-\text{CH}_2\text{PO}_3\text{H}_2$, $-\text{CH}_2\text{NR}_3^{20+}$ where R^{20} is an alkyl, or $-\text{CH}_2\text{NAr}_3^{x+}$ where Ar^x is an aromatic (arene), to provide a cation or anion exchange membrane.

5 Further still, the aromatic moiety may contain a hydroxyl group which can be readily elaborated by existing methods to generate $-\text{OSO}_3\text{H}$ and $-\text{OPO}_3\text{H}_2$ cationic exchange sites on the polymer. Ion exchange sites of the type stated may be provided as described in WO95/08581.

10

Preferably, said first conductive polymer is sulphonated. Preferably, the only ion-exchange sites of said first conductive polymer are sites which are sulphonated.

15

References to sulphonation include a reference to substitution with a group $-\text{SO}_3\text{M}$ wherein M stands for one or more elements selected with due consideration to ionic valencies from the following group: H, NR_4^{y+} , in which R^y stands for H, $\text{C}_1\text{-C}_4$ alkyl, or an alkali or alkaline earth metal or a metal of sub-group 8, preferably H, NR_4^+ , Na, K, Ca, Mg, Fe, and Pt. Preferably M represents H. Sulphonation of the type stated may be provided as described in WO96/29360.

25

Unless otherwise stated in this specification, a phenyl moiety may have 1,4- or 1,3-, especially 1,4-, linkages to moieties to which it is bonded.

30

Said polymer may include more than one different type of repeat unit of formula I; more than one different type of repeat unit of formula II; and more than one different type of repeat unit of formula III.

effected via sulphur atoms on respective chains. Alternatively, said polymer may be cross-linked via sulphonamide bridges as described in US 5 561 202. A further alternative is to effect cross-linking as described
5 in EP-A-0008895.

However, for polymers according to the invention described herein which are crystalline (which some are) there may be no need to effect cross-linking to produce a
10 material which can be used as a polymer electrolyte membrane. Such polymers may be easier to prepare than cross-linked polymers. Thus, said polymer of the inventions described herein may be crystalline. Preferably, said polymer is not optionally cross-linked as described.

15

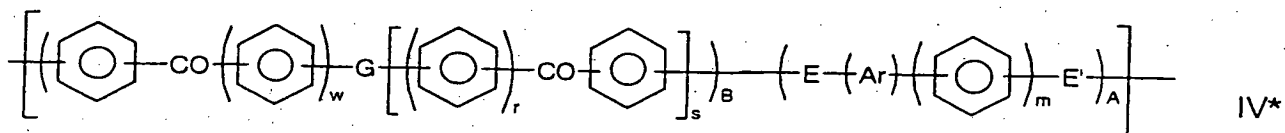
Where w and/or z is/are greater than zero, the respective phenylene moieties may independently have 1,4- or 1,3-linkages to the other moieties in the repeat units of formulae II and/or III. Preferably, said phenylene
20 moieties have 1,4- linkages.

Preferably, the polymeric chain of the polymer does not include a -S- moiety. Preferably, G represents a direct link.

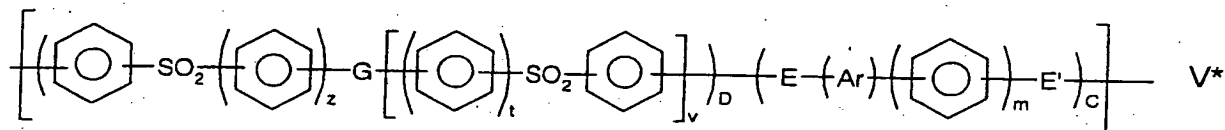
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Suitably, "a" represents the mole % of units of formula I in said polymer, suitably wherein each unit I is the same; "b" represents the mole % of units of formula II in said polymer, suitably wherein each unit II is the same;
30 and "c" represents the mole % of units of formula III in said polymer, suitably wherein each unit III is the same. Preferably, a is in the range 45-100, more preferably in the range 45-55, especially in the range 48-52.

As an alternative to a polymer comprising units IV and/or V discussed above, said polymer may be a homopolymer having a repeat unit of general formula

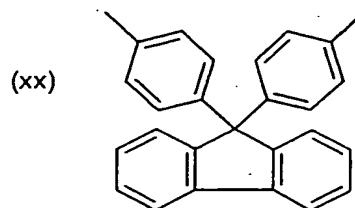
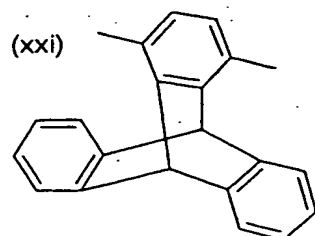
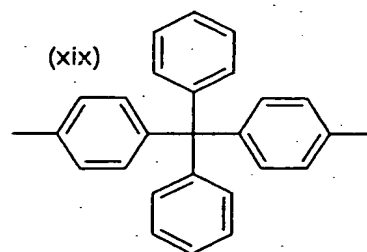
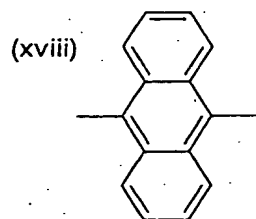
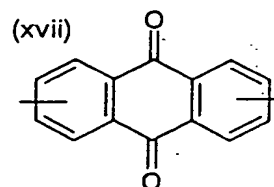
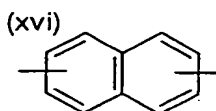
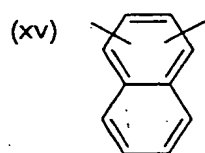
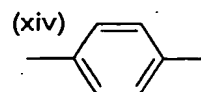
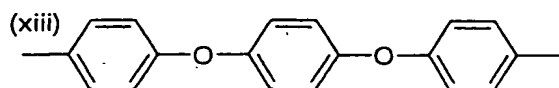
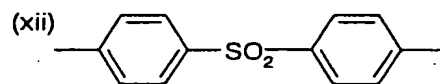
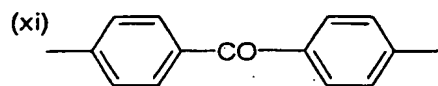
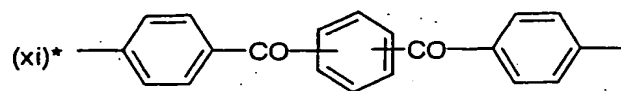


5 or a homopolymer having a repeat unit of general formula



or a random or block copolymer of at least two different units of IV* and/or V*, wherein A, B, C, and D independently represent 0 or 1 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

15 Preferably, m is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, r is in the range 0-3, more preferably 0-2, especially 0-1. Preferably t is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, s is 0 or 1. Preferably v is 0 or 1. Preferably, w is 0 or 1. Preferably z is 0 or 1.

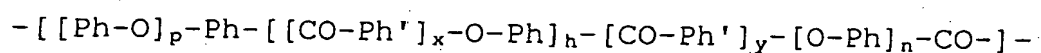


In (xi)*, the middle phenyl may be 1,4- or 1,3-substituted.

represents 0, w represents 0, s represents 1, r represents 1 and A and B represent 1.

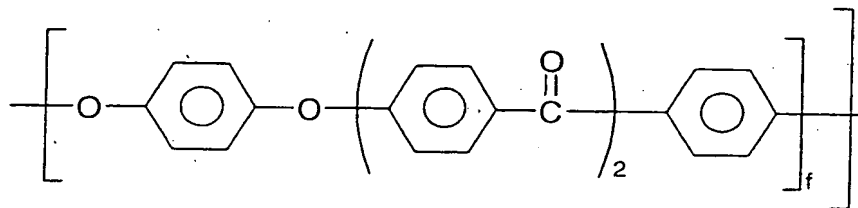
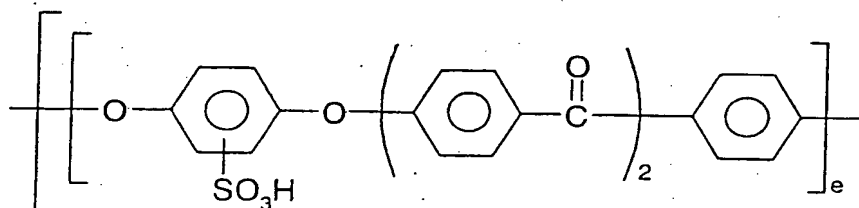
Referring to formula V, preferably, said polymer is not a polymer wherein: Ar represents moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents zero, z represents 1, v represents zero and C and D represent 1.

10 Preferably, said polymer is not a sulphonated aromatic polyetherketone of formula



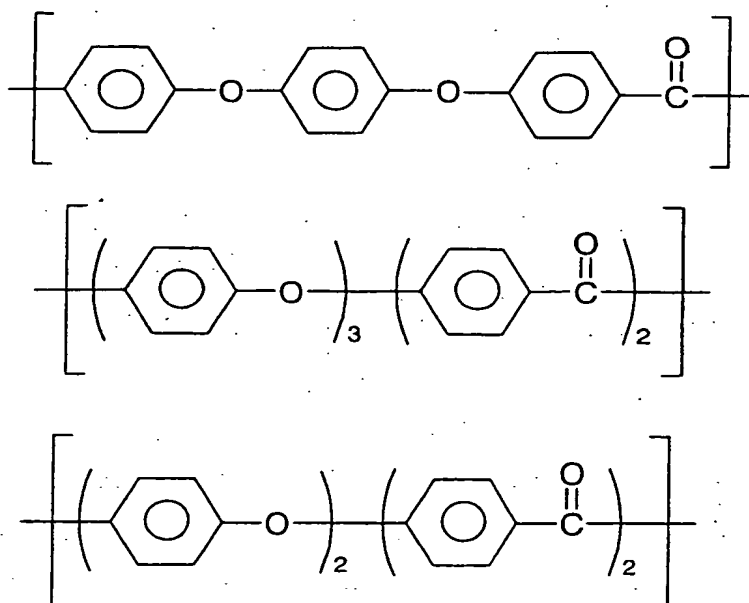
15 where Ph represents a 1,4- or 1,3- phenylene moiety; Ph' represents phenylene, naphthylene, biphenylene or anthrylene; p is 1, 2, 3 or 4; x, h and n are, independently, zero or 1; and y is 1, 2 or 3.

20 Preferably, said polymer does not conform to the formula



where

15



Suitable moieties Ar are moieties (i), (ii), (iv) and (v) and, of these, moieties (i), (ii) and (iv) are preferred. Preferred moieties Ar are moieties (xi), (xii), (xiv), (xv) and (xvi) and, of these, moieties (xi), (xii) and (xiv) are especially preferred. Another preferred moiety is moiety (v), especially, moiety (xvi). In relation, in particular to the alternative polymers comprising units IV* and/or V*, preferred Ar moieties are (v) and, especially, (xvi).

Preferred polymers include an electron-rich, relatively non-deactivated, easily sulphonatable unit, for example a multi-phenylene moiety or a fused-rings aromatic moiety, such as naphthalene. Such an easy to sulphonate unit may be sulphonated under relatively mild conditions to introduce two sulphonate groups per unit. Thus, preferred polymers may have at least 10π electrons in a delocalized aromatic moiety. The number of π electrons may be 12 or less.

of structure (i), m represents zero, A represents 1, B represents zero;

(c) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1 and C and D represent 1;

(d) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; or

(e) a unit of formula V wherein E and E' represents an oxygen atom, Ar represents a structure (i), m represents 0, C represents 1, Z represents 1, G represents a direct link, v represents 0 and D represents 1;

and a second repeat unit which is selected from the following:

(f) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents zero, A and B represent 1;

(g) a unit of formula IV wherein E represents an oxygen atom, E' is a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represent 1, A and B represent 1;

(h) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a

repeat unit of formula V* wherein Ar represents a moiety of structure (v), E represents a direct link, E' represents an oxygen atom, G represents a direct link, z, v and m represent 0, C and D represent 1.

5

Said polymers having repeat units IV* and V* may include any of repeat units (a) to (i) described above.

In some situations, polymers which include at least one repeat unit of formula IV or formula IV* may be preferred.

10

Copolymers may be prepared having one or more first repeat units and one or more of said second repeat units.

Where said polymer is a copolymer as described, the mole% of co-monomer units, for example said first and second repeat units described above, may be varied to vary the solubility of the polymer in solvents, for example in organic solvents which may be used in the preparation of films and/or membranes from the polymers and/or in other solvents, especially water.

20

Preferred polymers suitably have a solubility of at least 10% w/v, (especially at least 10% w/w) preferably a solubility in the range 10 to 30% w/v (especially in the range 10 to 30% w/w) in a polar aprotic solvent, for example NMP, DMSO or DMF. Preferred polymers are substantially insoluble in boiling water.

25

First units of the type described above (with the exception of units (a) and (c)) may be relatively difficult to sulphonate, whereas second units of the type described may be easier to sulphonate.

30

solution. IV is measured at 25°C on a solution of polymer in concentrated sulphuric acid of density 1.84gcm³, said solution containing 0.1g of polymer per 100cm³ of solution.

5 The measurements of both RV and IV both suitably employ a viscometer having a solvent flow time of approximately 2 minutes.

10 The main peak of the melting endotherm (T_m) for said polymer (if crystalline) may be at least 300°C.

15 In general terms, said composite membrane is preferably substantially stable when used as a PEM in a fuel cell. Thus, it suitably has high resistance to oxidation, reduction and hydrolysis and has very low permeability to reactants in the fuel cell. Preferably, however, it has a high proton conductivity. Furthermore, it suitably has high mechanical strength and is capable of being bonded to other components which make up a membrane electrode assembly.

20 Said polymer may comprise a film, suitably having a thickness of less than 1mm, preferably less than 0.5mm, more preferably less than 0.1mm, especially less than 0.05 mm. The film may have a thickness of at least 5µm.

30 Said polymer electrolyte membrane may comprise one or more layers wherein, suitably, at least one layer comprises a film of said polymer. Said membrane may have a thickness of at least 5µm and, suitably, less than 1mm, preferably less than 0.5mm, more preferably less than 0.1mm, especially less than 0.05mm.

said support material may be greater than 2000. Thus, said support material may comprise a polymer having moieties I, II and/or III or a homopolymer or copolymer comprising units IV and/or V.

5

Preferably said support material is selected from the following homopolymers of formula IV:

- E and E' represent oxygen atoms, G represents a direct
10 link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1

- E represents an oxygen atom, E' represents a direct
link, Ar represents a moiety of structure (i), m
15 represents zero, A represents 1, B represents zero

- Ar represents a moiety (iv), E and E' represent oxygen
atoms, G represents a direct link, m represents 0, w
represents 0, s represents 1, r represents 1 and A and
20 B represent 1.

- Ar represents a structure (i)*, E represents an oxygen
atom, E' represents a direct link, m represents 0, A
represents 1, B represents 0.
25

- Ar represents moiety (i), E and E' represent oxygen
atoms, G represents a direct link, m represents zero, w
represents 1, r represents 0, s represents 1 and A and
B represent 1
30

A said porous support material may be provided by a fabric which may have warp and weft strands or may comprise an irregular arrangement of fibres. Suitably, said pores are defined by the void volume of the fabric -
5 that is between the fibres. However, the fibres of the fabric themselves may be porous and penetrated by said conductive polymer. Alternatively, a said porous support material may be microporous and may suitably be made by a phase inversion process as hereinafter described. Such a
10 microporous material preferably has no through pores and/or contains no closed pores.

Preferably, said support material and said conductive polymer are in intimate contact. Whilst the two materials
15 preferably do not together define a homogeneous material, the support material and conductive polymer preferably intermingle (as would happen if, for example a surface of the support material was dissolved and contacted with said conductive material) in a boundary region between the two
20 materials.

The use of support material as described may allow polymers of lower equivalent weights (EW) (for example less than 800g/mol, less than 700 g/mol, less than 600 g/mol,
25 suitably less than 500 g/mol, preferably less than 450 g/mol or even less than 400 g/mol or 370 g/mol) or relatively inflexible and/or brittle polymers to be used as said conductive polymer in said composite membrane.

30 The composite membrane suitably includes a catalyst material (preferably a layer of a catalyst material) which is, suitably a platinum catalyst (i.e. platinum containing) or a mixture of platinum and ruthenium, on both sides of

Said composite membrane may be for a fuel cell or an electrolyser.

In addition to the utility of the composite membranes described herein as ion-exchange membranes for electrochemical fuel cells, the following further utilities are also contemplated:

1. Proton exchange membrane based water electrolysis, which involves a reverse chemical reaction to that employed in hydrogen/oxygen electrochemical fuel cells.
2. Chloralkali electrolysis, typically involving the electrolysis of a brine solution to produce chlorine and sodium hydroxide, with hydrogen as a by-product.
3. Electrode separators in conventional batteries due to the chemical inertness and high electrical conductivity of the composite membranes.
4. Ion-selective electrodes, particularly those used for the potentiometric determination of a specific ion such as Ca^{2+} , Na^+ , K^+ and like ions. The composite membrane could also be employed as the sensor material for humidity sensors, as the electrical conductivity of an ion exchange membrane varies with humidity.
5. Ion-exchange material for separations by ion-exchange chromatography. Typical such applications are deionization and desalination of water (for example, the purification of heavy metal contaminated water), ion separations (for example, rare-earth metal ions, trans-uranium elements), and the removal of interfering ionic species.
6. Ion-exchange membranes employed in analytical preconcentration techniques (Donnan Dialysis). This technique is typically employed in analytical chemical

Suitably the conductive polymers herein are blended with 0-40wt%, preferably 0-20wt%, more preferably 0-10wt%, especially 0-5wt% of other polymeric materials. Preferably, however, a blend of polymers is not provided.

5

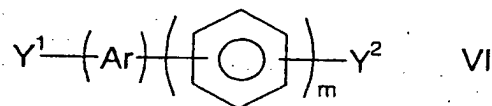
According to a third aspect of the invention, there is provided a fuel cell or an electrolyser (especially a fuel cell) incorporating a polymer electrolyte membrane according to the first or second aspects. The fuel cell may be a hydrogen or direct methanol fuel cell.

10

Polymers having units I, II, III, IV, IV*, V and/or V* may be prepared by:

15

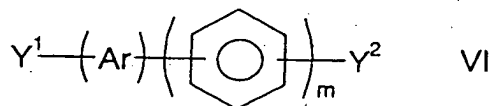
(a) polycondensing a compound of general formula



with itself wherein Y^1 represents a halogen atom or a group -EH and Y^2 represents a halogen atom or, if Y^1 represents a halogen atom, Y^2 represents a group E'H; or

20

(b) polycondensing a compound of general formula



In some situations, the polymer prepared, more particularly phenyl groups thereof, may be optionally substituted with the groups hereinabove described after
5 polymer formation.

Preferably, where Y^1 , Y^2 , X^1 and/or X^2 represent a halogen, especially a fluorine atom, an activating group, especially a carbonyl or sulphone group, is arranged ortho-
10 or para- to the halogen atom.

Preferred halogen atoms are fluorine and chlorine atoms, with fluorine atoms being especially preferred. Preferably, halogen atoms are arranged meta- or para- to
15 activating groups, especially carbonyl groups.

Wherein the process described in paragraph (a) is carried out, preferably one of Y^1 and Y^2 represents a fluorine atom and the other represents an hydroxy group.
20 More preferably in this case, Y^1 represents a fluorine atom and Y^2 represents an hydroxy group. Advantageously, the process described in paragraph (a) may be used when Ar represents a moiety of structure (i) and m represents 1.

25 When a process described in paragraph (b) is carried out, preferably, Y^1 and Y^2 each represent an hydroxy group. Preferably, X^1 and X^2 each represent a halogen atom, suitably the same halogen atom.

30 Compounds of general formula VI, VII and VIII are commercially available (eg from Aldrich U.K) and/or may be prepared by standard techniques, generally involving Friedel-Crafts reactions, followed by appropriate

The conductive polymer may be associated with the support material in a variety of ways. The method may involve laminating conducting polymer and support material together. Preferably, however, the method involves
5 impregnating porous support material with said conductive polymer.

Said porous support material may be a fabric or a microporous membrane.

10

Where said porous support material is a fabric, the method may include a step of contacting the fabric with a first solvent formulation comprising a first solvent and a conductive polymer, wherein the conductive polymer is
15 preferably dissolved in the first solvent. Said fabric may, therefore, be impregnated with said formulation. Thereafter, said first solvent may be removed, leaving said conductive polymer in pores of said fabric.

20

Said first solvent and said porous support material may be selected so that said first solvent solubilises, to some degree, a surface of the support material. Said first solvent may be capable of dissolving the support material to a level of at least 5wt%. This may improve
25 contact between the conductive polymer and said support material. Optionally, said first solvent may be capable of functionalizing (e.g. sulphonating) said support material to provide ion-exchange site on a surface thereof as hereinbefore described.

30

Said first solvent may be a polar aprotic solvent, for example NMP, or may be a protic solvent. A polar aprotic solvent may not be capable of solubilising said porous

solvent which will not substantially attack the polyetheretherketone, but may dissolve to some extent the conductive polymer already in the pores. In another embodiment, polyetherketone (e.g. PEKTM) may be used in the process described instead of polyetheretherketone. In this case, the polyetherketone is dissolved by the sulphuric acid, but not surface sulphonated. Otherwise the process is as described for the treatment of polyetheretherketone.

10

In another embodiment, the first solvent may be a polar aprotic solvent (e.g. NMP) in which, suitably, a conductive material (e.g. SPEDEK/PEKES) is provided, and said support material is a material (e.g. polyetheretherketone, especially PEEKTM, suitably as a fabric) which is not solubilized by said solvent, so that, suitably, the surface of said support material is not solubilized. In a further embodiment, the first solvent may be a polar aprotic solvent (e.g. NMP) in which, suitably, a conductive material (e.g. SPEDEK/PEKES) is provided, and said support material is a microporous membrane suitably made of a material (e.g. polyetherketone, especially PEKTM) which is not solubilized by said solvent, so that suitably the surface of said support material is not solubilized.

Where said support is a microporous membrane, preparation of the membrane may include a step of contacting a support material as described herein with a solvent formulation comprising said first solvent. Said first solvent preferably solubilizes the support material. Subsequently, the method preferably includes the step of contacting the support material with a second solvent.

30

between pores. Optionally, a said conductive polymer may be provided in said third solvent, thereby to penetrate pores in said support material. Said third solvent is preferably a polar aprotic solvent. NMP is a suitable solvent. Thereafter, the third solvent is evaporated.

The method may include a subsequent step of associating a catalyst material with the composite membrane prepared as described.

A said composite membrane described herein may be used in fuel cells or electrolyzers and, accordingly, the invention extends to a fuel cell or electrolyser incorporating a composite membrane as described.

Any feature of any aspect of any invention or embodiment described herein may be combined with any feature of any aspect of any other invention or embodiment described herein.

Specific embodiments of the invention will now be described, by way of example, with reference to figure 1 which is a schematic representation of a polymer electrolyte membrane fuel cell.

The abbreviation NMP referred to means N-methylpyrrolidone.

PEEK™ and PEK™ are trade marks of Victrex Plc for polyetheretherketone and polyetherketone respectively.

In the specification sulphonated polyether(biphenyl)etherketone is referred to as SPEDEK;

The polymer of Example 1 was sulphonated by stirring each polymer in 98% sulphuric acid (3.84g polymer/100g sulphuric acid) for 21 hours at 50°C. Thereafter, the reaction solution was allowed to drip into stirred deionised water. Sulphonated polymer precipitated as free-flowing beads. Recovery was by filtration, followed by washing with deionised water until the pH was neutral and subsequent drying. In general, ^1H nmr in DMSO-d₆ confirmed that 100 mole% of the biphenyl units had sulphonated, giving one sulphonic acid group, ortho to the ether linkage, on each of the two aromatic rings comprising the biphenyl unit, giving an Equivalent Weight of 583.

15 Example 3

Membranes were produced from the polymer from Example 2 after sulphonation as described in Example 2 by dissolving the polymer in N-methylpyrrolidone (NMP) at a concentration of 15% w/w. The homogeneous solution was cast onto clean glass plates and then drawn down to give 400 micron films, using a stainless steel Gardner Knife. Evaporation at 100°C under vacuum for 24 hours produced membranes of mean thickness 40 microns.

25

Example 4

The substrate, a piece of PEEK™ fabric having a thickness of 70µm and weight/unit area of $1.7 \times 10^{-3} \text{g.cm}^{-2}$ was clamped in a 10 cm diameter circular frame and immersed in a 15% (w/w) solution of SPEDEK/PEKES(1:1:5) prepared in Example 2 in NMP. The wetted substrate was placed in vacuum oven at 105°C for 1.5 hrs to remove the

The MEA using the unreinforced membrane punctured after 30hrs, whereas the reinforced composite membrane continued operating for over 400 hrs.

5 Example 6

The substrate, a 150 mm by 130 mm piece of PEEK™ fabric as described in Example 4 was clamped to a glass plate, impregnated with a 10% (w/w) solution of the
10 SPEDEK/PEKES prepared in Example 2 in 98% sulphuric acid and immediately immersed in de-ionized water. The composite membrane was dried then coated using a Doctor Blade with a coating of a 15% (w/w) solution of
15 SPEDEK/PEKES prepared in Example 2 in NMP, to 100 µm wet thickness and dried. Compared to the unreinforced membrane described in Example 3 which was highly swollen and fragile after immersion in boiling water for 1 hour, the composite membrane was strong and flexible.

20 Example 7

The procedure described in Example 6 was followed except that instead of coating with SPEDEK/PEKES in NMP, the composite membrane was coated with NMP alone, left for
25 30 minutes and dried. Compared to the unreinforced membrane described in Example 3 which was highly swollen and fragile after immersion in boiling water for 1 hour, the composite was strong and flexible.

30 Example 8

A 10% (w/w) solution of PEK™ (Grade P22, obtained from Victrex Plc, UK, having a Melt Viscosity of 0.22 kN sm⁻²)

Example 10

A 10% (w/w) solution of PES was dissolved in 98% sulphuric acid and was cast onto a glass plate to produce a 100 μ m wet thickness coating. The plate was immersed in deionized water, removed, dried under vacuum at 105°C, thereby producing a microporous membrane. This membrane was then impregnated with a 15% (w/w) solution of SPEDEK/PEKES prepared in Example 2 in NMP to produce a wet thickness of the solution of 250 μ m, followed by drying for 20 hours at 105°C. Compared to the unreinforced membrane described in Example 3 which was highly swollen and fragile after immersion in boiling water for 1 hour, the composite membrane was strong and flexible.

15

Example 11

The substrate, a 10 cm by 10 cm piece of PTFE fabric was clamped to a glass plate, impregnated with a 5% (w/w) solution of the SPEDEK/PEKES polymer prepared in Example 2 in NMP/methanol (30:70; w/w) and immersed in de-ionized water. The composite membrane was dried then coated using a Doctor Blade with a coating of a 5% (w/w) solution of SPEDEK/PEKES polymer prepared in Example 2 in NMP/methanol (30:70; w/w), to 250 μ m wet thickness and dried. The coating procedure was repeated. Compared to the unreinforced membrane described in Example 3 which was highly swollen and fragile after immersion in boiling water for 1 hour, the composite membrane was strong and flexible.

30

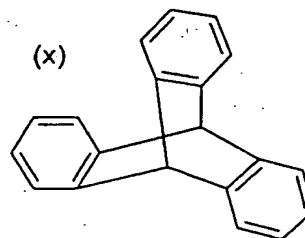
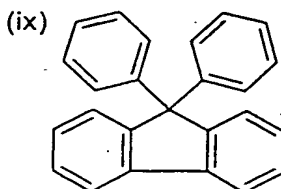
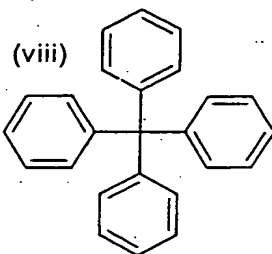
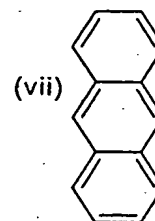
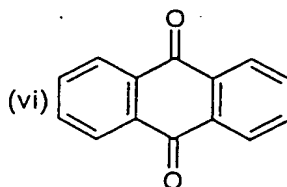
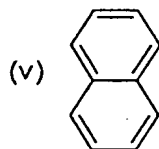
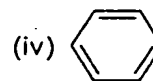
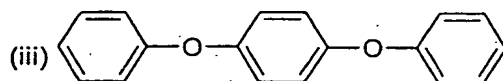
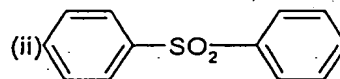
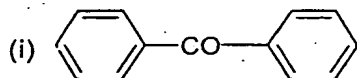
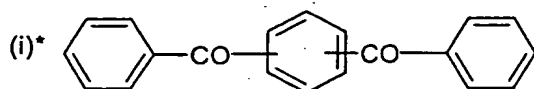
Example 12

each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extend to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

where Ph represents a phenyl group and Ar is selected from one of the following moieties (i)* and (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties

5



2. A membrane according to claim 1, where said first conductive polymer is sulphonated.

moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1;

5 (b) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero;

10 (c) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1 and C and D represent 1;

15 (d) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; or

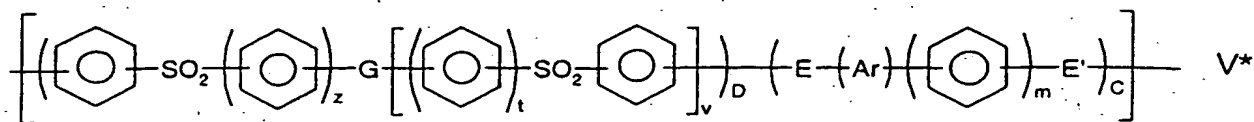
20 (e) a unit of formula V wherein E and E' represents an oxygen atom, Ar represents a structure (i), m represents 0, C represents 1, Z represents 1, G represents a direct link, v represents 0 and D represents 1;

25 and a second repeat unit which is selected from the following:

(f) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents zero, A and B represent 1;

30

(g) a unit of formula IV wherein E represents an oxygen atom, E' is a direct link, G represents a direct link, Ar



or a random or block copolymer of at least two different units of IV* and/or V* wherein A, B, C and D independently represent 0 or 1.

5

9. A membrane according to any preceding claim, wherein said first conductive polymer includes a biphenylene moiety.

10. A membrane according to any preceding claim, wherein said first conductive polymer includes a -O-biphenylene-O-moiety.

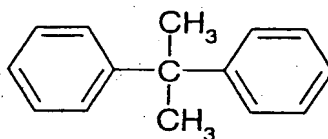
11. A membrane according to any preceding claim, wherein a film of said conductive polymer is laminated to the support material.

12. A membrane according to any of claims 1 to 10, wherein the support material is porous and said conductive polymer is impregnated in the support material.

13. A membrane according to any preceding claim, wherein said support material comprises a polymer having a moiety of formula I, II and/or III as described in any preceding claim except that the polymer of the support material is either not sulphonated (or otherwise functionalised to provide ion-exchange sites) or is only sulphonated (or otherwise functionalised to provide ion-exchange sites) at or in the region of the surface of the support material.

- a homopolymer of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; and is selected from:
- 5 - polysulphone for example comprising a homopolymer of formula V wherein E and E' represent oxygen atoms, m represents zero, C and D represent 1, z represents 1, G represents a direct link, v represents zero and Ar represents a moiety of structure:

10



- 15. A membrane according to any preceding claim, wherein said first conductive polymer has an equivalent weight (EW) of less than 800g/mol, preferably less than 500 g/mol.

- 16. A conductive polymer and a support material for the polymer, wherein said polymer includes:
 - 20 polyaryletherketone and/or polyarylethersulphone units; and units of formula $-O-Ph_n-O-$ (XX) wherein Ph represents a phenyl group and n represents an integer of 2 or greater and wherein Ph groups of units (XX) are sulphonated.

- 25 17. A fuel cell or electrolyser incorporating a composite membrane according to any preceding claim.

- 18. A method of making a composite membrane according to any of claims 1 to 16, the method comprising causing a
 - 30 conductive polymer as described in any of claims 1 to 16

24. A method according to claim 18 or claim 19, the method including:

5 contacting said support material with a solvent
 formulation comprising a first solvent which
 solubilizes the support material; and
 contacting the support material with a second solvent
 to cause phase inversion and render said support
 material porous.

10 25. A method according to claim 24, wherein said
 conductive polymer is provided in a third solvent and
 caused to penetrate pores in the support material.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/03449

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G65/48 C08J5/22 H01M6/18 H01M10/40 H01M8/10
H01M2/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C08J H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 574 791 A (HOECHST AG) 22 December 1993 (1993-12-22) cited in the application. claims 1-19 page 7, line 35 - line 45 page 8, line 41 - line 44	1-5, 9, 10, 12, 17-19
P, X	WO 00 15691 A (CHARNOCK PETER ; VICTREX MFG LTD (GB); WILSON BRIAN (GB); KEMMISH D) 23 March 2000 (2000-03-23) claims 1-35 page 21	1-12, 15-19



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

* & * document member of the same patent family

Date of the actual completion of the international search

7 December 2000

Date of mailing of the international search report

09. 01. 2001

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INTERNATIONAL SEARCH REPORT

national application No.
PCT/GB 00/03449**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-25 (all in part)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/GB 00/03449

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